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PROPOSED MODIFICATION TO LITHIUM BATTERY TEST SPECIFICATIONS
A Report Presented to ICAO October 1989

MAY 8 1990

Prepared for

Transportation Development Centre
Policy and Coordination Group

Transport Canada

by

Electrochemical Science and Technology Centre
University of Ottawa (ESTCO)

January 1990

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G. W. Allvey

Electrochemical Science and Technology Centre
University of Ottawa (ESTCO)

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The contents of this report reflect the views of the author and are not necessarily the official views or opinions of the Transportation Development Centre of Transport Canada.

Un sommaire en français de ce rapport est inclus avant la table des matières.

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16. Abstract

Prior to suggesting rules covering the air transportation of lithium rechargeable batteries, the current ICAO regulations relating to primary batteries have been reviewed. The latter regulations fail to address hazard potential as a function of cell design.

The main influences of cell design and electrical performance capability are enunciated in this study. In consequence, it is proposed that ICAO adopt a modified set of regulations which govern the air transportation of lithium batteries - albeit with additional specific test acceptance criteria for rechargeable batteries.

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16. Résumé

La réglementation de l'OACI concernant le transport aérien des générateurs rechargeables a été examinée avant de proposer une réglementation sur le transport aérien des accumulateurs au lithium. La réglementation de l'OACI ne tient pas compte des dangers possibles qui peuvent découler de la construction même des générateurs considérés.

Le présent rapport établit les principaux facteurs touchant la construction des générateurs électriques et les performances dont ils sont capables. Il est donc proposé que l'OACI adopte les modifications élaborées concernant le transport aérien des générateurs électriques au lithium, avec la réserve que les générateurs rechargeables soient soumis à des tests d'acceptation supplémentaires.

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Accumulateurs, piles, lithium, primaire, secondaire, OACI, réglementation sur le transport aérien.	Le Centre de développement des transports dispose d'un nombre limité d'exemplaires.

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SUMMARY

Regulations governing the air transportation of lithium cells/batteries are detailed in the ICAO and IATA handbooks. The criteria, described in these handbooks, relating to the packaging and modes of carriage of lithium batteries pertains specifically to primary (i.e. non rechargeable) cells/batteries. The growing presence of secondary (i.e. rechargeable) lithium cells/batteries within the marketplace prompted Transport Canada to seek guidance on 1) the possible hazards that may be associated with these newer types of batteries, and 2) the types of evaluation tests that should be performed in order to classify such batteries for possible carriage/use on board aircraft. In order to reduce the problems in transporting Canadian-made rechargeable lithium battery products, Transport Canada sought suggestions on methods of classification of such products.

The existing ICAO rules for air transportation of lithium cells/batteries were established on the premise that the hazardous potential of such products is dependent solely on the quantity of lithium contained within the cell and the nature of the cathode material employed. No consideration has been given to the design or construction of the individual cell and this was regarded as a major shortcoming of the regulations. Rather than building upon the above set of rules, to accommodate lithium rechargeable cells/batteries and thus propagating the above mentioned deficiencies, it was decided that it would be preferable to modify the above mentioned requirements such that cells/batteries could be classified according to their performance capabilities. In so doing, lithium batteries could be treated as a single group with specific additional tests imposed for the rechargeable versions - a mode of operation obviating the need to continually review new lithium-based electrochemical couples.

In addition to the author's long and varied experience in the battery industry - especially those years devoted specifically to the design and development of lithium cells - advice was sought from:

a) Office of Hazardous Goods Transportation (U.S. D.O.T.)- mainly responsible for the original transportation rules for lithium-based batteries,
b) U.S. D.O.D. - the largest customer of lithium type batteries worldwide,
c) CALPA & COPA - carriers of batteries,
d) NEMA representatives - representing Duracell, Eveready and Wilson Greatbatch (U.S. manufacturers),
e) Moli Energy - Canadian manufacturer of rechargeable lithium batteries,

f) Sanyo & Matsushita - primary/secondary battery manufacturers in Japan.

Apart from explosions, the main hazards associated with lithium cells/batteries reside in the toxicity or flammability of issued material when a cell vents. For the most part, this material will be in the fluid phase and be comprised essentially of 1) the starting electrolyte, 2) electrolyte plus reaction product or 3) electrolyte plus thermal decomposition product. In consequence, we have sought to recognize material hazards together with cell design variations in formulating a new acceptance and classification set of rules.

The evolved 'proposed rules' require that cells/batteries be subjected to prescribed evaluation tests. Cells/batteries are subsequently classified into various groups for air carriage dependent upon the outcome of these tests. These 'proposed rules' were critically reviewed by representatives of the North American manufacturing industry prior to the October 1989 meeting of ICAO. Duracell, Eveready and Wilson Greatbatch agreed to the objective, the process and the test procedure of the proposed rule restructuring. Moli Energy also agreed to the new proposals with one reservation. The latter company felt that a 'crush' test, as defined in our proposals, was too severe. Nonetheless, the 'crush' test was considered by us to be vital in assessing a cell's detrimental behaviour under conditions wherein the cell develops an internal short circuit. The main limitations of our proposal would appear to be due to the lack of information available, within the literature, concerning toxicity data of various electrolyte components. This, however, is pertinent to any set of rules - present or future.

As indicated above, the proposed rule revisions were reviewed at the October 1989 ICAO meeting. Seemingly, ICAO expressed interest in this proposed 'rules revision' as presented by Mr. M. Sastre (Manager, Dangerous Goods, Transport Canada) but decided that this forum was not sufficiently competent to make a judgement. It was therefore decided that the proposals will be placed before the UN commitee and ICAO will adopt any subsequent UN rulings.

SOMMAIRE

La réglementation concernant le transport aérien des piles et accumulateurs au lithium est contenue dans les manuels de l'OACI et de l'IATA, et les critères qui y sont définis concernent exclusivement la construction et le transport des piles, c'est-à-dire les générateurs électriques non rechargeables. Or, l'apparition en nombre de plus en plus élevé d'accumulateurs au lithium (c'est-à-dire de générateurs rechargeables) sur le marché a poussé Transports Canada à s'informer: 1) sur les dangers possibles associés à ce type nouveau de générateurs électriques et, 2) sur les essais d'acceptation à prescrire dans le but de les classifier dans l'optique de leur éventuel transport aérien. Pour atténuer les problèmes que pourrait poser le transport des accumulateurs au lithium fabriqués au Canada, Transports Canada a consulté diverses autorités concernant les méthodes de classification à adopter.

La réglementation de l'OACI concernant le transport aérien des piles et accumulateurs au lithium est fondée sur l'hypothèse que le danger qu'ils pouvaient représenter dépend uniquement de la masse de lithium qu'ils comportent et de la matière formant la masse cathodique. Ni la conception ni la construction des piles n'avait été prise en considération, ce qui fait que la présente réglementation comporte une importante lacune. Plutôt que d'étendre la réglementation actuelle aux accumulateurs au lithium et perpétuer la lacune précitée, il a été décidé qu'il serait préférable de modifier la réglementation de manière à pouvoir classifier ces accumulateurs, en fonction de leurs caractéristiques particulières. Ainsi, les générateurs au lithium pourront être considérés comme un groupe à part, dont seules les versions rechargeables seraient soumises à des tests supplémentaires, obviant ainsi à l'obligation de devoir examiner tous les générateurs au lithium, au fur et à mesure de leur apparition.

En plus de l'auteur reconnu pour sa longue expérience dans le domaine concerné - notamment dans la conception et la réalisation de couples au lithium - les organismes suivants ont été approchés:

a) Office of Hazardous Goods Transportation (ministère des Transports des É.-U.), à l'origine de la réglementation concernant le transport des générateurs au lithium;

b) Le ministère de la Défense des É.-U., le plus gros consommateur au monde de ce type de générateurs électriques;
c) l'Association canadienne des pilotes de ligne et la Canadian Owners & Pilots Association, à titre de transporteurs;
d) la NEMA à titre de représentante de Duracell, Eveready et Wilson Greatbatch (É.-U.);
e) Moli Energy, fabricant canadien de générateurs rechargeables au lithium;
f) Sanyo et Matsushita, fabricants japonais de générateurs rechargeables et non rechargeables.

Outre le risque d'explosion, le grand danger associé à ces générateurs réside dans la toxicité et l'inflammabilité des matières pouvant s'écouler à l'extérieur, la plupart sous forme de solution. Ces matières seront essentiellement constituées: 1) de l'électrolyte, 2) de l'électrolyte et du produit de la réaction chimique ou 3) de l'électrolyte et d'une matière résultant d'une thermolyse. Il a donc fallu déterminer chacun des dangers possibles en fonction des caractéristiques des générateurs considérés lors de l'élaboration des éléments de réglementation concernant la classification et l'acceptation de ces générateurs.

D'après la nouvelle réglementation proposée, tous les générateurs électriques doivent subir des tests d'évaluation. Ils seront ensuite classifiés, du point de vue de leur transport aérien, en catégories déterminées par le résultat desdits tests. En Amérique du Nord, les associations de fabricants concernées ont examiné cette réglementation d'un oeil critique, avant la date de l'assemblée de l'OACI prévue pour octobre. Duracell, Eveready et Wilson Greatbach ont signifié leur accord avec les objectifs, les modalités et les procédures préconisées par la réglementation amendée, de même que Moli Energy mais ce dernier avec une réserve. A savoir la trop grande rigueur de l'essai d'écrasement prévu que, pourtant, nous considérons comme essentiel pour déterminer le comportement réel d'un générateur dans des conditions de court-circuit interne. La réglementation proposée semble connaître des limites attribuables surtout à l'insuffisance de l'information disponible concernant le danger chimique que peuvent présenter les divers constituants des générateurs électriques. Mais, à ce chapitre, elle ne diffère en rien de toutes les autres réglementations, actuelles ou futures.

Comme il est dit plus haut, les modifications apportées à la réglementation en vigueur ont été examinées lors de l'assemblée de l'OACI tenue en octobre 1989. Apparemment, l'OACI s'est montrée intéressée par les modifications proposées par M. Sastre (directeur, Transport des marchandises dangereuses, Transports Canada) mais, ne se considérant pas suffisamment compétente en la matière, l'assemblée a décidé de soumettre les propositions à un comité des Nations Unies, dont la décision sera adoptée d'emblée par elle.

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1.0 INTRODUCTION

In consequence of the attractive specific energies and energy densities that appear attainable with lithium-based battery systems, the latter are being used/proposed for an ever increasing range of applications. The use of low rate cells in watches, calculators and heart pacemakers is now commonplace whilst higher rate cells, used in the camera industry, is well beyond its infancy. Lap-top computers, cellular telephones, safety survival equipment and a host of other such applications are in the throes of changing to lithium based power sources in order to achieve high energy packages with a minimum weight/volume penalty. In view of the forthcoming proliferation of lithium battery usage, a need exists to review the rules governing the general carriage of such batteries.

There are two particular concerns: passengers unwittingly carrying on board aircraft equipment which contains lithium cells/batteries, and the desire of manufacturers to transport their products as quickly as possible to the marketplace.

Transport Canada commissioned this study in an attempt to better understand the developments and progress made over the past ten years or so within this industry. Such information would allow an evaluation of hazards associated with different lithium cell designs and chemistries, the knowledge gained being instrumental in modifying the existing transportation regulations concerning such products. Updating transportation regulations in light of the design improvements achieved over the past decade could result in the reduction of restrictions placed on the shipment of Canadian made products without compromising safety. Canadian manufacturers of secondary (rechargeable) versions of the lithium-molybdenum disulphide and lithium-manganese dioxide chemistries are handicapped by the present transportation rules.

The methodology adopted for this exercise was as follows:

(a) Review battery design criteria and how it relates to safety.

(b) Review existing rules governing transportation of lithium cells/batteries.

(c) Discuss existing rules and experiences with interested parties, e.g.,

1. regulatory authorities
2. manufacturing industry
3. carriers
4. users

(d) Propose test criteria which will immediately categorize cells/batteries into groups for appropriate shipment.

2.0 RULES

The current transportation rules governing the shipment of lithium cells/batteries and exercised by ICAO (1) and IATA (2), are based largely on the U.S. DOT E 7052 (3) document which was formulated in the mid to late 70s. In turn, the latter U.S. document was founded almost entirely on particular applications by specific users, during the early to mid 70s, of the lithium-sulphur dioxide products. In consequence, the rules currently existing within ICAO's handbook were written around a specific high rate lithium chemistry technology that was prevalent some 15 years ago. As such, the existing rules neither reflect the changes made over the past decade or so to the design of lithium-sulphur dioxide cells/batteries, nor do they reflect all the characteristic differences attainable with other lithium based chemistries.

Early vintage cells were prone to leakage and sometimes explosion. Much of the leakage could be attributed to inadequate cell sealing and/or corrosion problems associated with: a) the venting device, b) the electrical feed through material, c) the type of glass insulator employed around the electrical feed through. Explosions may be attributed to abusive use in association with the relative amounts of active electrode materials, or failure of the venting device to operate at the designed pressure. In particular, one manufacturer persevered with a heat sensitive venting mechanism for some years. The latter system relied on a bead of solder which sealed a hole in the cell top. Provided that heat was conducted rapidly to all parts of the cell, the method worked. Unfortunately, this is not the case and, therefore, results were somewhat erratic. The two companies involved in lithium-sulphur dioxide cell production in those days then developed (in sequence) 'beer can' type vents, i.e., weakened sections which yield and crack at predetermined pressures. One system worked quite well and reliably whilst the other was subject to blockage and therefore occasionally presented a hazardous condition.

In the field of lithium-sulphur dioxide cell/battery technology, the industry over the past decade has made substantial improvements leading to a much more reliable product. These improvements may be summarized:

(a) The use of the 'beer can' type vent (4) - suitably positioned to allow consistent trouble free operation.

(b) The use of TA23 glass - developed by Sandia Labs - as an electrical feed through insulator. This glass formulation was the first to exhibit good corrosion resistance and expansion characteristics compatible with the neighbouring metal.

(c) The use of molybdenum as electrical feed through material instead of tantalum, to reduce corrosion effects (5).

(d) The 'balanced' cell involving electrochemical equivalent amounts of lithium and cathode material. This arrangement theoretically ensures that the two active materials within the cell become spent simultaneously and obviate the possibility of hazardous secondary reactions occurring.

Whilst nobody claims to have all the answers with respect to possible causes of the occasional explosion, the above improvements have led to an impressive safety record with large volume users who claim that their cell failures have fallen to less than ten cells per million (6). It may be assumed that the actual failures are higher than those quoted and that some failures are not reported. It would follow, however, that unreported failures are of a minor nature and may well pass unobserved. It is significant that none of the reported failures occurred during aircraft transit.

It is further argued that the minimum voltage requirement of 2 volts or 2/3 of the original cell voltage - see ICAO packing instruction 406 or DOT E 7052, para.3 - is also outdated (7,8).

The requirement dates back to the problems associated with one manufacturer, in particular, referred to above. The argument presented here is not that the test procedure, outlined in packing instruction 406, is totally outdated but that much of the premises on which it is based has been superceded. It will be shown later that the characteristics of lithium chemistries and cell construction techniques result in very different

performance capabilities. As such, any hazard potential should not be judged solely on the weight of lithium present in the cell. A cell containing less than 0.5gm. of lithium and employing very high surface area electrodes but exhibiting poor thermal conductivity properties can be far more dangerous than a cell with, say 2gm. of lithium, and employing very low surface area electrodes and good thermal conductivity properties.

A further contradiction occurs between the labelling requirements given in the ICAO handbook with those in the DOT E 7052 document. One requires 'dangerous when wet', whilst the other requires 'flammable solid' labelling. These conflicting requirements cause confusion to shippers/carriers and considerable complications for a mixed transit (say road haulage followed by air transit). Whilst every elementary chemistry textbook will cite lithium's reactivity with water, it is often overlooked that such demonstrations are invariably performed in a large excess of water. Under the latter conditions, the lithium speeds around on the surface of the water buoyed on a bubble of hydrogen - similar to the hovercraft principle. Any heat generated ignites the hydrogen produced by the lithium-water reaction, resulting in the occasional flame or pop. When water is applied to lithium cells, the reaction can be the same but the observations are quite different. Firstly, water could only enter the cell quite slowly - even supposing a damaged cell case - and the lithium is in excess. Since the solubility of lithium hydroxide is only 4 molar, the rate of the lithium-water reaction is self limiting. Secondly, liquid cathode systems create a deposit on the lithium surface. This salt deposit would be the first material to dissolve in the water - seldom producing hydrogen in any quantity - prior to the interaction between lithium and water. For these reasons, most manufacturing dry rooms are equipped with water sprinklers to combat any lithium cell/battery fires. In consequence, it is suggested that labelling requirements should be standardized to read 'flammable solid'.

Other areas that cause manufacturers, users and shippers/carriers confusion centres on the national prerogatives to allow special dispensations. In the U.S. alone over 100 companies ship under exemption E 7052, but additional exemptions involving air transportation have been

issued under E8457, E8978, E9348, E9355 and E9703. Apart from increasing the paperwork in reviewing each submission prior to awarding an exemption, there are no clear cut guidelines on which manufacturers should base their tests, and of course their submissions. The latter is particularly true for lithium rechargeable cells/batteries wherein no such class is described in the ICAO handbook. Whilst the handbook does not refer specifically to lithium primary cells/batteries, the test requirements, etc. either imply primary batteries or are seriously lacking if applied equally to rechargeable cells/batteries.

In view of the above, it would seem pertinent to suggest updating the rules and requirements governing the transportation of lithium cells/batteries. The update should obviously cover both primary and secondary cells/batteries and indicate specific differences where it is deemed necessary.

Whilst the overall objective would be to establish lithium battery transportation rules which are similar to those of lead-acid, nickel-cadmium and zinc alkaline batteries, etc., it is reckoned that too much apprehension still exists concerning the safety of lithium batteries, to take such a large step. To obviate the need to establish a multitude of classes covering the many lithium chemistries available and the assortment of construction designs, a slightly different approach will be adopted than heretofore. This approach would assess and categorize batteries based on their performance characteristics.

In brief, all lithium cells and batteries, up to a certain size, will be subjected to a series of tests - not unlike those already existing in the ICAO handbook. The outcome of these tests will be:

(a) the cell/battery explodes;
(b) the cell/battery vents flammable dangerous goods;
(c) the cell/battery vents products which are toxic/flammable;
(d) the cell/battery vents products which are not harmful;
(e) the cell/battery maintains its integrity and behaves benignly.

At this stage, it is suggested that the dangers of lithium cells/batteries per se may be isolated, and further tests/assessments are used to classify an offending material as toxic or flammable - using the packaging instructions already in existence.

For example, cells/batteries identified in (a) above would not be allowed on any aircraft. Similarly, batteries within item (b) should only be allowed in air transportation in accordance with an exemption from the appropriate competent national authority. Items in (c) would follow the appropriate packaging instructions for toxic/flammable fluids. Items (d) and (e) would be classified as 'non hazardous' products.

Manufacturers would be responsible for ensuring that tests are performed diligently and for maintenance of these records - for auditing purposes by the national D.O.T. agencies. Test records should include all details of the tests performed and observations together with a copy of the complete manufacturing drawings of the cell/batteries tested. The complete file of the tests should be placed in an envelope, dated and sealed such that a visiting D.O.T. inspector is assured that he is the first person to break the seal.

By applying the assessment criteria, manufacturers can quickly classify their products for transportation purposes. Likewise, forwarders or users may use the same classifications and are immediately bound to follow the packaging instructions already existing within the ICAO handbook.

3.0 CONTRIBUTIONS

As indicated previously, viewpoints concerning rules (present and future) governing the transportation of lithium cells/batteries, were sought from various interested parties. The Canadian Airline Pilots Association were receptive to being guided in this matter by better qualified specialists. Their main apprehension concerning changes in transportation rules is the possibility of a less competent company manufacturing and shipping questionable product and causing a hazard (Appendix 1). The viewpoint is undeniably valid; however, no matter which rules are in force, there will always be, regrettably, someone who will -either wittingly or not - breech those rules. The author is aware of companies that currently occasionally breech rules in order to expedite delivery.

The Canadian Owners and Pilots Association had very little comment to make except that they didn't want rule changes that would then be revoked soon afterwards. The latter comment referring to the late 1970s when they were instructed to carry lithium powered 'Emergency Locator Beacons'. The instruction was reversed about a year or so later - at some cost to their members.

The Office of Hazardous Materials Transportation (U.S. DOT) seemingly recognize that improvements to lithium cell/battery designs have occurred over the past decade and that the existing rules are ready for some modification. However, this office is inundated in reviewing applications for exemptions (new or renewal) under the present system and lacks the necessary resources to plan anything different for the future.

We are greatly indebted to the NEMA committee - representing North American battery producers - for their support and constructive criticisms in the derivation of our proposals. Whilst the general philosophy of the proposals - given later - is that of the Canadian group, the tests described and acceptance criteria were evolved by mutual agreement. It follows therefore that the suggestions made herein are generally accepted and agreed by the North American battery manufacturers. Individual manufacturers may not be in total agreement. Moli Energy Ltd. for example, agree with the test regime except for

the 'crush' test. They feel that the latter test is too severe but, as yet, they have not suggested an alternative means of simulating an internal short circuit within a cell.

Sanyo and Matsushita had no significant offerings - this presumably because their rechargeable cells are very small and they ship under the present (<0.5gms.) rulings. Both companies are apparently not considering the production of rechargeable cells any larger than their present button (or coin) sizes.

Battery Engineering Inc. limited their comments to their observations regarding the problems of shipping product. Seemingly, their main problems arise from the inconsistency of labelling requirements and the confusion of shipping personnel in interpreting the various regulations in force.

Views were not sought from Transport Canada since they sponsored this review. It was assumed that they would be receptive to the findings whatever the outcome.

A copy of a visit report is included in appendix 2. This report was written immediately after returning from the visits referred to.

4.0 CELL DESIGN

On the basic premise that the cell is the weak link in a battery chain, it would appear pertinent to review cell designs, characteristics and susceptibilities in order to understand failure modes and possible resultant consequences. Test regimes are established which probe the latter weaknesses and are used to assess the cell's vulnerability. The latter practice is commonplace and merely reiterated so that the reader will make the comparison between the weaknesses listed below and the suggested test methods described later.

Irrespective of the chemistries employed or the many cell shapes and sizes available, there are basically two types of mechanical design, viz:

Type 1. High power capability. Electrodes tend to be of thin cross section but possessing a large surface area. Typically this class of cells embraces:

(a) Jelly roll format in cylindrical cell cans
(b) Multiplate format in prismatic cell cases, and
(c) Multidisc electrodes in coin shaped cells.

The latter tends to be used rarely because it incurs a high production cost.

Type 2. High energy but low power capability. In this case the electrodes tend to be thick but possessing limited active surface area. Cells will consist mainly of:

(a) two concentric electrode cylinders within a cylindrical case, or
(b) two disc electrodes within a coin shaped cell.

As indicated above, the two mechanical designs are used to achieve a high power capability or a high energy (low power)
capability - they are general principles and therefore not specific to lithium based cell/battery systems.
Properties which are specific to lithium couples will be covered below.

Cathodes used in lithium systems fall into two main classes, viz:

(a) Solid cathodes, i.e. cathodes constructed and behaving in a manner similar to conventional cells

(b) Liquid cathodes, i.e. the solid part of the cathode is only a reaction site or current collector. The active cathode ingredient is present within the electrolyte solution. In this case, the cathode reacts spontaneously with lithium and deposits reaction product on the lithium surface - this deposit then prevents further chemical corrosion of the lithium (i.e. the lithium surface is passivated until electrical energy is taken from the cell).

Generally speaking, the solid cathode systems exhibit electrochemical rate determining properties which are slower than those of liquid cathodes. This translates into liquid cathodes delivering greater power (higher current densities) than solid cathodes and operating more efficiently at lower temperatures.

The whole issue becomes complicated when permutations between cathode types and build standards are considered (9,10). Such 'mix and match' procedures are commonplace in an attempt to achieve specific cell/battery properties. Similarly, liquid cathode solutions are used wherein the electrolyte exhibits an extremely high impedance. The latter in combination with a low power build design (type 2 above) yields a safe, high energy, low power cell which is commonly used for memory protection devices or powering electronic clocks.

The above remarks serve to illustrate the fallacy of assessing the safety characteristics merely on whether the cell has a liquid or solid cathode. The only generality that is possible between solid or liquid cathodes is that solid cathodes will employ electrolytes that are likely to be more flammable than toxic, whilst liquid cathodes tend to be more toxic than flammable. Thus, for transportation purposes, it would seem prudent to devise a standard set of test criteria against which any and all cells/batteries are measured. It is the intent of this exercise to establish a proposal for such a test procedure and, to this end, a description of some of the more common failure modes are included in order to justify the specific test requirement.

4.1 Influence of current collection conductors. High power cells are frequently made wherein the lithium anode and the cathode material (or current collector) are supported on a substrate. The substrate material fulfills three main functions, namely:

(a) Provides strength to the composite structure
(b) Minimizes electrode electrical impedance
(c) Maximizes heat flow through the electrode and reduces the risk of 'hot spots'.

Substrates are typically comprised of expanded mesh, woven mesh, or wires but irrespective of the type used, they are subject to a cutting procedure during cell manufacture. Unless all edges of the substrate are coined, there is always the likelihood of some ragged edges - pointing in all directions and specifically at an angle to the plane of the substrate. Although such ragged edges may not be apparent in a new cell, they may become exposed during cell usage - when active material has been consumed and the active surface recedes. High power cells, in which the separator thickness is minimized, present the highest risk of these sharp edges piercing the separator and causing an internal short circuit.

Some cell systems employ little or no substrate in the lithium anode. Connection is often made by cold welding the lithium to a tab (say nickel) or directly to the cell case. The method is acceptable for electrode stacks that are tightly constrained in the cell case and cells that are subjected to low rate discharge and which are not exposed to excessive shock demands. Since lithium is a rather soft metal, the possibility exists whereby, during shock or vibration, the lithium tears away from the weld points or in fact the lithium buckles, the consequence of these movements either causing an internal short circuit or a 'hot spot' during a subsequent discharge..

The above indicates a need to subject cells/batteries to a searching vibration and shock regime to determine the cell's vulnerability to such conditions. A short circuit test must be incorporated to determine the hazard potential of the cell. Either due to a manufacturing defect or conditions of usage, some cells will undoubtedly fail by a short circuit mechanism.

It is further suggested that partially or fully discharged cells should be subjected to the same tests, the reasoning for the latter being that some electrode structures will become less robust during electrical discharge, i.e., either due to consumption of active material or the accumulation of reaction product within the electrode's pores causing embrittlement. A final consideration is the possibility of producing a metastable reaction product,i.e. one which may be shock or temperature sensitive and liable to rapid decomposition (11,12).

4.2 Influence of pack pressure. Pack pressure was briefly alluded to in the previous section and refers to the tightness of the active materials composite or the force exerted on the electrode surface. It will be evident that a loose pack (low pack pressure) will be susceptible to movement and possible damage during shock or vibration testing. Similarly, a tight pack means that the two electrodes of a cell are extremely close to each other and separated only by 'squeezed' separator material. Hence a tight pack is susceptible to any flaws contained/created in the separator material.

Pack pressure changes can occur from the moment that electrolyte is introduced into the cell at the factory, or during normal electrical usage of the cell. Quite obviously these changes occur as a result of shape changes in one or both electrodes. Such shape changes resulting from:

(a) In some cell systems, the electrolyte relaxes the binding of the cathode material and continues to permeate throughout the electrode. In such cases, considerable swelling of the cathode is observed.

(b) The volume occupied by reaction products is greater or less than that occupied by the initial reactants. Hence, the pack pressure either increases or decreases during electrical discharge. The change tends to be most notable in liquid cathode systems wherein the pack pressure reduces during discharge operations. For thin electrodes in a spirally wound configeration, the effect is minimized because the starting materials begin with only a very thin cross section and the electrode stack is tightly wound.

For bobbin cells the phenomenon is far more readily apparent and so is sometimes offset by the employment of springs which are designed to sustain a constant pack pressure and maintain a constant electrode gap.

(c) Secondary (rechargeable) cells will inevitably undergo shape change during repetitive electrical cycling due to (mainly) the solubility of materials and the fact that during recharge, material is redeposited quite randomly, i.e., material cannot be replaced exactly from whence it came. Cells, containing anodes which dissolve during discharge, invariably are subject to the formation of dendritic growth during a subsequent recharge. Thus, an electrode which begins life as a solid sheet, may, after a few cycles, take on a very sponge like appearance. Dendritic growths, as described, will 'seek out' flaws in the separator and result in the formation of an internal short circuit. Indeed, this is the normal failure mode for rechargeable cells which incorporate a soluble electrode.

Similarly, cathodes which are repetitively oxidised and reduced normally undergo changes in topography and possible weakening of the structure - again because during the recharge, the user has no control on the reaction sites on the electrode surface. The advantages of using intercallation compounds as cathode materials resides in their ability to accommodate reaction products within the interstices of the cathode lattice. In consequence, very little shape change occurs during electrical cycling of these materials.

4.3 Influence of vents. The inclusion of a venting device within the cell container structure is designed to protect the container against a possible rapid internal increase of pressure leading to an explosion. In order to be aware of the problems associated with venting devices, it would seem relevant to review the types of devices that are in operation together with their limitations. Whilst the venting devices themselves are pressure sensitive, they tend to be designed to operate at specific temperatures. More specifically, it should be remembered that lithium melts at a temperature of 180 deg.C. At such temperatures, lithium becomes more mobile and can quite easily cause internal short circuits. Furthermore,

spontaneous exothermal reactions may be experienced - especially with liquid cathode systems - in conjunction with a rapidly replenished liquid surface, the latter events leading to a thermal 'runaway' condition. Another consideration is that of the separators, many of which may begin to soften at these elevated temperatures and lose their strength and separator properties.

To be safe, venting devices are therefore designed to operate at temperatures in the range 130-150 deg.C, i.e., reasonably well below the lithium melting point. In order to achieve sufficient internal pressure to initiate a vent, the designer tends to use the following parameters:

(a) The vapour pressure of the solvent, or main constituent of the electrolyte.

(b) The vapour pressure of a decomposition product.

(c) Either of the above in combination with the dead space volume within the cell.

For liquid cathode systems, the main constituent is the cathode material itself. Since the material is being consumed during discharge, it is necessary to design the venting device solely around the pressure that the cathode vapour will exert at a temperature of about 140 deg.C. This is relatively simple for the lithium-sulphur dioxide couple since the vapour pressure of sulphur dioxide, at these temperatures, is approximately 450 p.s.i. (32kg/sq.cm.). Thionyl chloride, sulphuryl chloride, etc., exhibiting lower vapour pressures tend to be more difficult and necessitate vent operation at about 160 p.s.i. (11.3 kg/sq.cm.). In the latter cases, the problem is further compounded by the fact that these chemistries are normally produced within stainless steel hardware.

Solid cathode systems differ marginally in that during electrical discharge, the fluid component of the cell is not being consumed and the 'dead space' volume remains sensibly constant. The Moli Energy cell (lithium-molybdenum disulphide) is completely filled with electrolyte, i.e., no 'dead space' volume. At temperatures of about 130 deg.C. the propylene carbonate (electrolyte solvent) thermally decomposes and creates a

hydraulic pressure of about 350 p.s.i. (24.7 kg/sq.cm.) thus, their venting device is designed to open at this order of magnitude.

Venting devices basically rely on the incorporation of a weakened section within the cell hardware structure and is normally achieved by:

(a) A coined section of metal within the cell container, such that small distortions in the vicinity of the coined area will cause cracking or tearing.

(b) Mounting the glass-to-metal feedthrough within thin walled metal. Any bowing of the metal creating a fissure at the glass to metal interface.

(c) Puncturing of a thin diaphragm by means of bowing the diaphragm against a sharp point, or pushing the diaphragm away from a fixed point (e.g. a weld point), and creating a tear (13,14). The problems most frequently encountered with venting devices tend to be:

    (1) Reliability of operation. This applies principally to low pressure systems in stainless steel hardware. Reproduceability, during high volume production, is difficult to maintain when using very thin materials. Material which is slightly thicker than the norm - or possibly work hardened during processing - can lead to vent operation at pressures much higher than intended.

    (2) Clogging of an opened vent. During the venting operation, the vent opens correctly but is subsequently plugged by separator or electrode material. The effect is almost the same as not having a vent in that pressure is finally relieved by emission of the clogging agent or by bursting the container.

Not all cells require the inclusion of a vent, although such a statement continues to be a subject of controversy within the battery industry. Large diameter cells which are sealed by means of peripheral crimping of a plastic

insulator - particularly in cold rolled steel hardware - can (depending on wall thickness) undergo joint distortion at low pressures (in the order of 100 p.s.i. or 7.0kg/sq.cm.). These distortions damage the seal and provide a fluid leak path, thus obviating the need for a dedicated venting system.

Very low rate cells, i.e. of limited power capability, are also available without vents. It is reckoned that even under short circuit conditions, the internal temperatures and pressures will not attain dangerously high levels. Such cells are normally totally safe unless exposed to a very high temperature environment, i.e., heated by a neighbouring fire. Under the latter conditions, even a sealed container of water would react like a bomb.

4.4 Influence of cell size. A sometimes overlooked phenomenon is that of the thermal management changes associated with scaling up cells. This remark is concerned primarily with spirally wound cells wherein cells of different radii are made using the same electrode procedure and the same vent design but perform differently. An example may be a 'AA' sized cell and a 'C' sized cell that discharge at the same current density but exhibit different voltage/temperature profiles. The quick answer resides in the fact that in scaling up, the volume of the cell (and therefore, the total energy or power capability) can double whilst the radius (and therefore the cell container surface area) only increases to 140%. Furthermore, the electrode tabbing material and dimensions may be the same in each case. Thus, for two cells operating at the same current densities, heat dissipation is more rapid within the smaller radius cell. These observations are submitted to explain why localized 'hot spots' in larger cells can be far more devastating in that higher temperatures can be attained and higher heating rates experienced. In theory, although seldom in practice, venting devices should be designed to operate at lower pressures for the larger diameter cells.

4.5 Influence of overdischarge/recharge. Although the mechanisms and the chemistry involved are not totally understood in any of the lithium systems that may be reviewed, observations indicate that overdischarging lithium cells and the electrical recharging of previously

discharged primary cells can result in dangerous consequences (6,15,16). Lithium rich cells during overdischarge can react spontaneously with electrolyte solvent decomposition products, whilst cathode rich cells give rise to spontaneous reaction between cathode and any lithium which is electrodeposited on the cathode (or current collector) surface. In both cases exothermal reactions can initiate a rapid internal heating. To minimize or obviate this effect, the so called 'balanced' cell was introduced, whereby lithium and its counter cathode are present in exact electrochemical equivalent proportions. Thus, in theory, the two materials become spent simultaneously.

The electrical recharging of previously discharged cells can lead to similar situations as those described above. Redeposited lithium will be finely divided, i.e. the redeposited lithium will have high surface area, and therefore be extremely reactive. Thus, it can react quickly with any oxidising agent present and cause rapid heating. A further possibility is that the deposited lithium will form dendritic growths which will ultimately lead to internal short circuits.

Whilst the above comments are targetted towards lithium primary cells, similar properties and behaviour patterns would be observed with lithium secondary or rechargeable cells with a few minor differences. Lithium secondary cells will invariably be produced initially with a large excess of lithium anode. This excess represents the substrate upon which lithium is deposited during electrical recharge. To a lesser extent, this excess of lithium compensates for material which becomes electrically 'lost' during cycling, the 'lost' material being present within the sludge that will gradually appear within the cell.

Secondary cells - particularly those involving a soluble electrode - will employ a much more substantial separator than used in its primary counterpart. Ideally, the separator should be sufficiently robust to impart physical separation between the electrodes, present little resistance to ionic diffusion but highly resistant to penetration by metallic growths emanating from the lithium electrode.

These differences encourage manufacturers to make certain recommendations regarding the treatment of their products and thus ensure safe and efficient usage. The main recommendations would centre on:

(a) Do not discharge beyond or below a certain voltage. This obviates the possibility of cells being overdischarged.

(b) Electrical recharges should be performed at relatively low current densities to a maximum specified voltage.

Recharge conditions will follow closely the principles used in smooth electrodeposition processes in that low current density deposition from a highly conductive solution will yield smooth plating. Conversely, deposition from low conductance solutions or high current densities will lead to spongelike deposits. The limiting end voltage is suggested to avoid the possibility of electrolyte decomposition.

Whilst the recommendations will achieve the desired result, they are capable of being followed in single cell applications only. Cells within multicell battery packs are seldom individually controlled and therefore subject to possible overdischarge or 'high voltage' charging.

The 'influences' listed above and the associated problems are not specific to lithium based batteries but apply in general to all battery systems - primary and secondary. Differences between conventional cells (e.g. Ni-Cd, Pb-acid, alkali manganese etc.) and lithium cells are ones of degree (i.e. chemical and physical properties of lithium) and of chemistry specifics, i.e., lithium cells are associated with unusual solvents which may be toxic or flammable.

5.0 CHEMISTRIES

Table 1 lists many of the lithium systems either in current production or in some stage of development. Although the list is not exhaustive, it serves to indicate the number of chemistries that could be in circulation in the near future and, hence, the number of characteristics, i.e., chemical properties plus different build standards that could be in being. This is one of the very reasons that lithium batteries - as a category - should be assessed on performance rather than weight of lithium or chemistry.

Similarly, Table 2 - again by no means exhaustive - is included to show the types of properties that will be found in components of lithium cells. For the most part, only the fluid components are of particular significance, since these will be the major constituents of any vented effluent. One point that the table highlights is the dearth of information available concerning the toxicity of many components. This is obviously a major setback when establishing safety criteria.

The literature refers to T.L.V.(short time exposure) values for certain materials. Basically, these values are the maximum concentration levels for safe operation when exposed to them for 15 minute sessions, for up to 4 times per day. Such a concentration would be a preferred standard when considering allowable exposures on an aircraft. Complete changes of air within an aircraft, at a sweep rate of 6 changes/hour, would mean that the concentration of any offending material would be substantially reduced within ten minutes and, therefore, substantially below the T.L.V.(STEL) at all times.

As stated above, the T.L.V.(STEL) values are not readily available for all the fluids that may be considered as components of the electrolyte, cathode or reaction/ decomposition products. For this reason, the ICAO (dangerous goods) committee may have to continue with the LC50 values. The problem in so doing is that the LC50 values are based upon a long exposure time (typically 14 days) and therefore tend to be of much lower numerical values. Whilst the lower numerical values are erring on

the safe side, one could foresee that batteries, which would pose little threat to aircrew or passengers, could be banned from air transit.

Throughout this review, the remarks have been directed principally to ambient temperature batteries of rather conventional construction. Other batteries which also contain lithium as anodic material may be described somewhat differently and therefore assessed under alternative standards. Examples of such battery systems are:

(a) Solid state batteries wherein all cell components are in the solid state. Such batteries are invariably harmless but may be assessed by the standards included herein.

(b) Thermal batteries wherein the cell components are in the solid state until required for use. Such batteries are inert until the electrolyte is melted and 'activation' is achieved by:

(1) heating a surrounding electric blanket, or

(2) firing a pyrotechnic device.

Both forms of the battery are totally inert but item (2) may be governed by the packing instruction for explosive devices.

(c) Reserve primary batteries wherein the electrolyte is physically separated from the active electrode materials. Under such conditions, the battery remains inert until the electrolyte is allowed to 'wet' the electrode surfaces. It should be noted that thermal batteries may also be classified as reserve batteries.

In cases where the electrolyte is transported separately from the battery, the battery itself presents little danger. Batteries in which the electrolyte cannot be physically removed and transported separately, should be subjected to the standards described herein.

TABLE 1.

LITHIUM BATTERY SYSTEMS

Primary systems

TYPE	CATHODE TYPE
Lithium/Sulphur dioxide	Liquid
Lithium/Thionyl chloride	Liquid
Lithium/Bromine chloride	Liquid
Lithium/Chlorinated sulphuryl chloride	Liquid
Lithium/Manganese dioxide	Solid
Lithium/poly carbon monofluoride	Solid
Lithium/Copper oxide	Solid
Lithium/Lead bismuthate	Solid
Lithium/Copper oxyphosphate	Solid
Lithium/Vanadium pentoxide	Solid
Lithium/Iodine	Solid
Lithium/Chromic oxide	Solid

Secondary systems

Lithium/Molybdenum disulphide	Solid
Lithium/Titanium disulphide	Solid
Lithium/Vanadium oxide	Solid
Lithium/Manganese dioxide	Solid
Lithium/Sulphur dioxide	Liquid

Table 2 CHEMICAL PROPERTIES

NR	USE	FLAMMABILITY/ COMBUSTABLE	EXPLOSIVITY	CORROSIVENESS	TOXICITY	STABILITY	CANCER CAUSING
3 acetonitrile	E.Sv.	flash p=6C/cc UEL: 16%,LEL: 3% autoign temp 524C	MI=yes SC=maybe	skin irritation	TLV-TMA=40ppm TLV-STEL=60ppm LC(50)=13mg/l odour threshold:24 ppm	react with water	mutagenic
1 acetylene black	C.C	combustable-exposed to heat	yes(dust)-exposed to heat	no	TLV-TWA= 3.5 mg/m3		cancer
3 aluminum chloride	E.Sv.	not flammable mp=192.7C	MI=no SC=no	yes	TWA=2 mg(Al)/m3 LD(50)= 3.7 g/kg	stable in air and light, reacts violently with water	mutagenic
bromine chloride	L.C.			yes	poisonous	oxidizer	
carbon monofluoride	S.C.				TLV-TWA=2.5mg/m3		
chromic oxide	S.C.	no	no	no	EL=0.5mg/m3 (as in Cr)	stable (avoid water) -reacts violently with Li'	possibly (Cr)
copper oxyphosphate	S.C.	-----					

Table 2 cont'd

HR	USE	FLAMMABILITY/ COMBUSTABLE	EXPLOSIVITY	CORROSIVENESS	TOXICITY	STABILITY	CANCER CAUSING
3 dimethylsulphoxide	E.Sv.	flash p=95C/cc UEL: 28.5% LEL:2.6% autoign 490F	MI-no SC-maybe	no	LD(50)=14,500 mg/kg TDLo=2,500 mg/kg	reacts with many compounds (avoid water)	mutagenic
2 dioxolane	E.Sv.	flash p= 2C extremely	under flames can be explosive	irritant	LC(50)=3000 mg/kg LD(50)= 3200 mg/kg	stable	no info
3 ethylene		UEL: 36% LEL: 2.7% flash p= -181C	under flames	no	LC(50)= 95 pph	stable	no info
ethylene carbonate	E.Sv.	flash p=143C			LD(50)=10g/kg	stable	no info
3 iron disulphide	S.C.	powder ignites in air			LDLo= 20 mg(Fe)/kg	instable -exposed to water	no info
3 iron sulphide	S.C.	violent reaction when exposed to Li at 260 C- fumes are toxic			LDLo= 20 mg(Fe)/kg	stable	no info
lithium	A	pyrophoric yes-exposed to heat or flames	yes-in air	no	LD(50)=1g/kg LC(50)=not available	instable-in air and water	no info
2. lithium bromide	E.Su.	no	no	irritant	LD(50)=1680mg/kg	stable (avoid water)	no info
3 lithium chloride	E.Su.	no	no	irritant	LD(50)=526mg/kg	instable in moisture	mutagenic
lithium hexa-fluoroarsenate	E.Su.	no	no	irritant	TLV-TWA= 2.5 mg(F)/m3 TLV-TWA= 0.2 mg(Ar)/m3 PEL-TWA= 2.5 mg(F)/m3 PEL-TWA= 0.01 mg(Ar)/m3	stable (avoid water)	Ar,F are potentially

Table 2 cont'd

HR		USE	FLAMMABILITY/ COMBUSTABLE	EXPLOSIVITY	CORROSIVENESS	TOXICITY	STABILITY	CANCER CAUSING
	Lix^{m}MoS2 (discharged intercalated cathode)	S.C	powder ignites	no	no	not available	stable in air and low humidity	no info
3	lithium perchlorate	E.Su.	maybe ignited by organics	no	irritant	not available	stable-except in heat	no info
3	manganese dioxide	S.C.	supports combustion	cat explosive reactions with a variety of O cpds	no	TLV-TWA= 1.72 ppm LD(50)= 422 mg/kg LDLo 45mg/kg	stable-except in heat	no info
	molybdenum disulphide	S.C.	no	explosive-potassium nitrate	no			genetic toxicology
1	propylene carbonate	E.Sv.	flash p 135C no	no	no	PEL-TWA= 100ppm LD(50)= 29g/kg	stable	suspected
3	sulphur dioxide	L.C.	no	no	to zinc	TLV-TWA= 2ppm TLV-STEL= 5ppm LC(50)= 2520ppm/H	stable	tumorigen teratogen
3	sulphuryl chloride	L.C.	no	yes-PbO2	yes- in water	TDLo=2850 mg/kg/ 1Y-I:ETA	instable-in water	tumorigen
D	teflon	B.	no	no	no	TDLo= 80mg/kg:ETA	stable	yes- when decomposed

Table 2 cont'd

HR	USE	FLAMMABILITY/ COMBUSTABLE	EXPLOSIVITY	CORROSIVENESS	TOXICITY	STABILITY	CANCER CAUSING
tetrahydrofuran	E.Sv.	flash p= -14C/cc UEL: 12% LEL: 1.5%	MI-no SC-maybe yes-in air yes-exposed to heat of flame	no	TLV-TWA= 200ppm TLV-STEL= 250 ppm odour threshold =2.543 ppm	instable-autoxidation in air	no info
3 thionyl chloride	L.C.	no	yes- to a variety of chemicals	yes to skin	TLV-TWA= 3 ppm(as Cl) LC(50)= 500 ppm/H	instable=in moisture and air	no info
3 vanadium pentoxide	S.C.	no	yes-LI	irritant	dust:TLV= 0.2 ppm :LD(50)= 10mg/kg :LCLo=70 mg/m3/2H fumes:TLV= 0.02 ppm	stable	mutagenic

LEGENDS

ACGIH	Conference of Governmental Industrial Hygienists
cat	catalyses
cpds	compounds
EL	exposure limit
ETA	equivocal tumorigenic agent=evidence of tumorigenic activity, pathological findings found, but with no mention of control animals
flash p	flash point
HR	hazard rating
I	intermittent administration of a chemical ie. once a day
LC(50)	lethal concentration-inhalation-killed 50% of animal population tested
LD(50)	lethal dose-all exposures except inhalation-killed 50% of animal population tested
LDLo	lowest dose of material introduced by any route other than inhalation over any period of time, reported to cause death to animal or man
LEL	lower exposure limit
MI	mechanical impact
no info	no information
O	oxidizing
OSHA	U.S. Occupational Safety and Health Administration , Department of Labor
PEL	permissible exposure limit-for air contaminants
pph	parts per hundred
ppm	parts per million
SC	static charge
STEL	short term exposure-per 15 min. no more than 4X/day with 60 min. between exposures
TDLo	lowest dose of a material introduced by any route other than inhalation over any period of time and reported to produce any toxic effect in humans or to produce carcinogenic, neoplastigenic or teratogenic effects in animal or humans
TLV	threshold limit value
TWA	time-weighted average-over 8 hours per day 5 days per week
UEL	upper exposure limit
Y	# of days of administration of the chemical to lactating mother after birth of off spring

LEGEND: FOR USES

A	anode
B	cathode binder
C.C.	cathode collector, esp. liquid cathodes
E.Su.	electrolyte solute
E.Sv.	electrolyte solvent
L.C.	liquid cathode
S.C.	solid cathode

LEGEND: FOR HAZARD RATING (HR)

HR= 1	SLIGHT OR MILD TOXICITY. produces changes in the human body which are readily reversible and which will disappear following termination of exposure
HR= 2	MODERATE TOXICITY. causes reversible changes in the human body but not severe enough to cause serious physical or health impairment or threaten life
HR= 3	SEVERE TOXICITY. causes irreversible changes in the human body sever enough to produce serious physical or health impairment or threaten life
HR= 0	INSUFFICIENT DATA AVAILABLE

6.0 RECOMMENDATIONS

The rules currently in force regarding the transportation of lithium cells/batteries were essentially derived in the late 1970s and were based upon the technology prevailing, within one or two manufacturers, at that time. In particular, the packing instruction, item 424 (DOC 9284.An/905), requiring cell/battery voltages to be greater than 2 volts or 2/3 of the voltage of the undischarged cell/battery, was formulated empirically on the experience of potential hazards occasioned by one manufacturer of lithium-sulphur dioxide products. During the past decade or so, design changes have resulted in a much safer product such that the above referenced requirement would now appear redundant. Similarly, cells/batteries have been categorized according to whether they:

(a) contain a liquid cathode
(b) contain a solid cathode
and (c) the weight of lithium contained in the anode.

It has been shown that the potential for a hazardous situation to occur should not be based upon the lithium content of the cell/battery but by its type of construction. The rate capability of the cell should be the criterion upon which safety assessments are made. The only real value associated with lithium loadings lies in the possibility of an experienced technologist being able to determine the equivalent loadings of cathode and (to a lesser degree) electrolyte. Such calculations enable the assessment of the toxicity and flammability hazards associated with these materials.

To some extent, it must be assumed that the improved safety record of lithium cells/batteries is already recognized by some countries by their relaxation of the ICAO regulations. As examples of the latter, one may cite the U.S. DOT who operate by way of their series of exemptions and, perhaps, Direction Generale de L'Aviation Civile (France) who include certain liquid cathode systems within their interpretation of packing instruction 406. In the latter case, they allow cells containing up to 12gms. of lithium, within packages containing up to 500gms. of lithium, to be carried aboard passenger

aircraft. To the author's knowledge, this practice has been in force for a minimum of three and a half years with no report of an incident.

It follows therefore, that some modification in ICAO's transportation regulations would be desirable wherein cells/batteries are regulated upon their performance capabilities rather than on chemical composition. Such changes to the regulations would centre upon knowing how a cell/battery system would respond to a preset group of tests/evaluations. Adoption of such a philosophy would allow secondary (rechargeable) lithium cells/batteries to be incorporated within the same general requirement structure as that of primary cells/batteries - albeit with rechargeable cells undergoing some additional testing. In consequence a new set of rules is proposed which seeks to:

(a) Simplify manufacturers' understanding of transportation criteria for their products

(b) Recognize technology improvements within the industry

(c) Standardize requirements within ICAO member countries

(d) Maintain safety assurances during the air transportation and use of lithium cells/batteries.

In developing the proposed revisions to the transportation regulations, a few assumptions have been made, viz:

(a) The largest battery pack that will be in common usage during the next few years will consist of 10 'D' sized cells. Such a pack is already in wide circulation/use by military agencies as a BA 5590 battery. EPIRBS (Emergency Locator Transmitter Radio Beacon) conforming to the new SARSAT (search and rescue satellite aided transmission) standards will also be using power sources of up to this size.

(b) In the event of a cell/battery failure occurrence during air transportation or usage, only one cell per aircraft will actually fail, vent and emit fluid. Statistically, it is virtually impossible to support this risk assessment although, of the millions of cells produced worldwide during the past 8-10 years,

very few incidents have been reported. Of the latter incidents, none have been reported during air transportation. The largest user organization of such cells quotes failure incidences of 0.0001% for lithium-sulphur dioxide systems, none of which occurred during air travel. It should also be noted that the latter organization uses a very high proportion of large (D sized or bigger) cells.

(c) The short circuit tests included in our proposed test requirements, whilst being extremely severe, are necessary in anticipation of a virtual eventuality. Whilst cells/batteries may pass the shock/vibration tests without apparent physical damage, the short circuit (or crush test) is incorporated to anticipate a future manufacturing flaw, or in the case of rechargeable cells, the normal failure mode.

Ironically, during 1989 three lithium battery manufacturers have made recalls on their products - all solid cathode systems -due to one unexpected incident in each case. The companies involved are Fuji (including Sanyo and Fujitsu), Duracell and Moli Energy. No serious personal injury was reported and the incidents did not occur during aircraft transportation - although without a doubt, the majority of cells/batteries had been transported by air at some stage. Duracell reported a design fault; Moli Energy attributed their problem to a production technique, and no statement has been seen from Fuji, although this also is likely to be attributed to a flaw in the manufacturing process or inadequate quality inspection procedures.

(d) Venting fluids are assessed on the basis of the toxicity hazard potential associated with concentrations resulting from the fluid - exiting the vented cell - diffusing into a ten cubic metre volume. The ten cubic metre volume represents an average cockpit section and, apart from lavatories, is the most confined part of the aircraft.

Alternatively, the free volume (cabin) per passenger could have been used - applying a fresh air sweep rate of 6 changes of air per hour (fresh air is introduced at a rate varying from 6 to 30 changes per hour). Such an approach

was considered to be less demanding than the above referenced 10 cubic metre volume.

(e) The proposed rule changes are part of a continuing exercise and therefore subject to further revision, during the next 5-10 year time frame, in light of increased knowledge and experience. Ultimately, it may be foreseen that regulations concerning lithium batteries will be reduced to requirements similar to the more conventional systems, e.g., dry cells, nickel-cadmium, lead-acid, etc. - albeit being cognisant of the toxic/flammable nature of some of the materials normally contained in lithium systems.

(f) Batteries containing greater than 25gms. of lithium are reckoned to be in limited demand, i.e., special applications only, for the foreseeable future. As such, it is suggested that manufacturers wishing to ship such large batteries should apply to the local regulatory authority for dispensation, the latter being a procedure that is already in practice. Indeed, the overall aim of these proposals has been to suggest changes to the existing rules only where such changes appear sensible and enhancing. No useful purpose is served by suggesting changes without reason.

A final recommendation is that of reviewing the labelling requirement 'Dangerous when wet' - which is not well founded and indeed, yields a false impression. A fire on board an aircraft is most likely to emanate from cargo in the vicinity of batteries rather than from the batteries themselves. Even supposing the fire was initiated within a cell/battery pack, the probability is that only a few cells - at most - would be responsible. In both cases, the immediate remedial action would be the provision of a large heat sink - that is to say, application of a profuse supply of cold water. A more appropriate label would be 'flammable solid' and such would be consistent with general road transportation requirements.

7.0 PROPOSED STANDARD

7.1 Purpose of Standard

The purpose of this standard is to define the requirements for the transportation of specified types of lithium cells and batteries. A further objective is the amendment of existing lithium battery transportation rules in light of the advancement in lithium cell/battery design and technology. Current rules have been constructed mainly around the use and transportation of primary (throwaway) cell/battery systems whereas the increasing use of secondary (rechargeable) battery couples necessitates the introduction of a similar set of regulations. The proposed regulations will embrace both primary and secondary batteries in a manner that will allow expeditious transport of product without compromising safety. The proposed test procedures and resulting rulings regarding battery cell transportation are outlined in Figures 1-7.

7.2 Conditions of Standards

7.2.1 Size of Cells and Batteries

Cells that are covered under this standard must not contain more than 6 grams of lithium if they are based upon a solid cathode system or 3 grams of lithium if they are based upon a liquid cathode system. The lithium weight expressed is that contained within an anode when it is in the fully charged condition. For electrochemical systems based upon a mixed (liquid and solid) cathode composition, the ruling will be as for liquid cathodes. Batteries comprising cells of either system (i.e. liquid or solid cathode) will not contain an aggregate quantity of lithium of more than 25 grams.

7.2.2 Construction

Cells covered by this standard must be hermetically sealed.

7.3 Definitions

7.3.1 The term "cell" as used in this context refers to a single encased electrochemical unit and one which exhibits a voltage differential across its two terminals.

7.3.2 The term "battery" refers to two or more cells which are electrically connected together whether or not they are contained in a single package, holder or container. Batteries may also include protective devices such as diodes, fuses, current limiters, etc.

7.3.3 "Hermetically sealed" means closed by fusion, gasketing, crimping, or equivalent means so that contained fluids cannot unintentionally escape.

7.3.4 The term "primary cell" refers to a cell which is designed to be electrically discharged only. Such cells are not capable of accepting an electrical recharge.

7.3.5 The term "secondary" or "rechargeable cell" refers to a cell which is designed to accept an electrical recharge after it has been previously depleted of energy.

7.3.6 A "fully charged cell" has the following meanings:

(a) for primary cells: The cell is in the same condition as manufactured, except for storage. The cell has not previously been used or electrically discharged.

(b) for secondary cells: The cell has been electrically recharged to restore all its electrical energy. Such recharging will be performed in a manner recommended by the manufacturer.

7.3.7 A "cycle" is the electrical discharge of a cell (to a stated depth of discharge (DOD), e.g. an 80% DOD cycle of the nominal capacity has been removed during the electrical discharge) to a load voltage of less

than 2/3 of its original open circuit voltage, followed by an electrical charge which restores it to its starting condition.

7.3.8 "Open circuit voltage" refers to the potential difference across the terminals of a cell/battery under a no-load condition (no current is being drawn).

7.3.9 "Short-circuit" is a direct connection between the positive and negative terminals of a cell/battery that provides a virtual zero resistance path for current flow.

7.3.10 Venting is the controlled emission of fluid (usually gaseous) from a cell in a manner designed by the cell manufacturer.

7.4 General Requirements

7.4.1 Test Frequency

The tests described in this standard shall be conducted prior to the first shipment or when significant cell or battery design changes are made. In absence of any design changes, the tests will be repeated every three years.

7.4.2 Sample Size

Cells. Ten (10) cells of the type to be transported shall be tested under each of the test conditions specified.

Batteries. Four (4) batteries of the type to be transported shall be tested under each of the test conditions specified.

7.4.3 Conditions of Sample Cells and Batteries

All sample cells/batteries will be in the fully charged state prior to the start of the test, unless specified otherwise.

7.4.4 Test Temperature

All tests shall be conducted at a temperature of 22°C, unless otherwise specified.

7.5 Draft Proposals

7.5.1 Group A

Non-hazardous cargo

Lithium cells and batteries that successfully pass all the tests as detailed below may be regarded as non-hazardous goods and transported freely by road, rail, sea, or air (including Passenger aircraft). The only restriction placed on the transportation of such goods being the requirement to satisfy the need to ensure that cells and batteries satisfy the conditions that they do not externally short circuit.

7.5.1.1 Test 1

Altitude simulation, thermal stability, short circuit

Condition of cells a) fully charged
b) fully discharged

(a) The cells/batteries must be stored for six hours at an absolute pressure of 11.6 kPa and at a temperature of 22°C 2°C.

(b) The cells/batteries must be exposed to a temperature of 75°C for a period of not less than 48 hours.

(c) The cells/batteries shall then be subjected to a short circuit current by connecting a conductor across the positive and negative terminals. The total resistance of the conductor will be not greater than 0.05 ohms and the temperature of the test will be 55°C. The cell shall remain connected to the discharge circuit for one hour after the case temperature has returned to the operational ambient temperature.

7.5.1.2 Test 2

Vibration, shock, short circuit

Condition of cells a) fully charged
b) fully discharged

a) The cells/batteries must be rigidly clamped to the platform of a vibration machine such that items are firmly held but none of their dimensions are altered. A simple harmonic motion having an amplitude of 0.8mm (1.6mm maximum total excursion) must be applied. The frequency must be varied at a rate of 1Hz/min between the limits of 10Hz to 55Hz. The entire range of frequencies and return must be traversed in 95 5 minutes for each of three mutually perpendicular mounting positions of the battery and two perpendicular positions of the cells. One of the directions of vibration must be perpendicular to the terminal face of the battery or cell. In the event that a resonance frequency is found, the cell/battery will be vibrated at this frequency for not less than three hours.

b) The cells/batteries will then be secured to the testing machine by means of a rigid mount which will support all mounting surfaces of the battery. Each cell/battery must be subjected to a total of three shocks of equal magnitude. The shocks must be applied in each of three mutually perpendicular directions. Each shock must be applied in a direction normal to the face of the battery. For each shock, the battery must be accelerated in a manner such that during the first 3 milliseconds the minimum average acceleration is 75g (where g is the local acceleration due to gravity). The peak acceleration must be between 125g and 175g.

c) The cells/batteries will then be subjected to a short circuit test by connecting a conductor across the positive and negative terminals. The total resistance of the conductor will not be greater than 0.05 ohms and the temperature of the test will be 55°C. The cell/battery shall remain connected to the

discharge circuit for one hour after the case temperature has returned to the operational ambient temperature.

7.5.1.3 Test 3

Applies to batteries consisting of paralleled cells

For this test, all cells should be in the fully charged condition except for all cells in one parallel string which should be in the fully discharged condition.

Repeat test 2 in its entirety.

7.5.1.4 Test 4

Crush test - Cell condition: new fully charged

This test is performed on single cells only.
The cell shall be deformed until its open circuit voltage drops abruptly or until it drops to at least one third of its original open circuit value - thus, indicating the development of an internal short circuit. The point of deformity should be on one long side of the cell, at a distance of one quarter the length of the cell measured from the cell bottom; that is to say, three quarters of the cell length from the cell top. The cell top being the surface wherein the cell is sealed.

The deforming force is applied by means of a vice, a hydraulic ram, or other similar means. The clamping plates of the vice (hydraulic ram or similar) shall be covered with a hard heat insulating surface such that heat is not transferred from the cell to the clamping device. To effect distortion, a 6mm dia rod (also covered with heat insulating material) will be placed between one jaw of the clamping plate and the cell. The main axis of the rod will be at right angles to the main axis of the cell. The force applied will be just sufficient to cause cell deformation and the initiation of an internal short circuit, i.e. the cell voltage falls abruptly. At the point wherein the voltage of the cell drops significantly, the applied force will be removed.

Acceptance criteria for meeting the requirements of Group A are:

(a) The cells/batteries must maintain their integrity during the tests defined. Some distortion, due to swelling is permissable. Mass leakage or evidence of melted parts is not permissable.

(b) Cell/battery weights after test should be within 0.1% of its starting weight.
Cells/batteries failing any tests outlined in Group A are further assessed within the requirements of Group B.

7.5.2 Group B

7.5 2.1 Controlled dangerous materials

This group of cells/batteries are those which would fail to meet any of the tests outlined in Group A. Whilst in itself such failures would not constitute a dangerous situation, the items warrant further assessment.
In consequence, the results obtained from the Group A tests will be used to determine the allowable mode of transportation. Criteria to be addressed will be :

1. toxicity of effluent fluids
2. flammability
3. cell explosivity

7.5.2.2 Toxicity

(a) The emission of any substance (as measured by cell weight loss) into a volume of $10m^3$ which results in concentrations lower than the T.L.V. (short term exposure) or the published LC50 values. Such cells/batteries will be regarded as non hazardous material and therefore allowed unrestricted transportation.

(b) Where such emissions yield concentrations greater than the T.L.V. (short term exposure) or LC50 values, cells/batteries will follow the rulings which apply to toxic materials. Thus, such cells/batteries will be treated as a class 6.1 material (ICAO) and abide by the requirements of packing group 2 or 3.

7.5.2.3 Flammability

Cells which emit fluids and which ignite during this venting operation, are not considered within this category. Such cells would require local national dispensation before being allowed on board aircraft.

7.5.2.4 Explosivity

Cells which explode under any of the test conditions defined above may not be transported by aircraft. An explosion is hereby defined as an instantaneous cell venting wherein solid matter from any part of the cell is propelled to distances greater then 25cms away from the cell. The test conditions to be adopted for this assessment are as follows.
A wire mesh cage will be positioned around the test cell such that the cell is distanced from any side of the cage by 25cms. The mesh will have a grid density of 6-7 wires per cm and consist of annealed aluminium wire of 0.25mms. diameter.
The cell will be judged to pass this test if it meets the following criteria:-

(a) No solid cell component shall travel completely through the screening.

(b) The indentation of any part of the surrounding mesh shall not exceed 1mm.

In the event that cells/batteries are determined to be hazardous in two or more of the above criteria, the most severe ruling will apply.

7.5.3 Group C

Equipment being transported

- i.e. not used in transit
- and incorporating one or more lithium primary batteries.

Such equipment will be classified for transportation purposes, identically to the classification of the battery showing the most potential hazard. The battery rating in Groups A and B will determine the allowable mode of transportation of the equipment.

7.5.4 Group D

Equipment (portable) employing lithium primary cells/batteries which is temporarily transported and may be used in transit.

Batteries within this group will be subjected to a forced discharge test.

Forced discharge test:

Cells within these batteries will be in the fully charged condition except for one cell in each series connected string. This one cell will be completely discharged. Note: for paralleled connected batteries each series connected string will contain one completely discharged cell. Batteries will be subjected to the conditions of Test 2 parts a) and b) prior to the forced discharge. The battery will then be discharged (if possible) under resistive load conditions such that the average current draw is not less than 10% below the rating of the battery protective devices (fuses, current limiters etc). The discharge will be terminated when the battery terminal voltage is less than one third of the original open circuit voltage. Batteries will be observed for a further period of 24 hours after removal of the load.

The findings of this test will be used to categorize the battery into Group A or B again using the ruling of the "most potential hazard". In other words, batteries within this category cannot be classified in Group A if it compromises cells from Group B. Such batteries must be classified as Group B batteries.

7.5.5 Group E

Rechargeable lithium cells/batteries
- transportation only

Cells/batteries within this group will be subjected to the tests outlined in Group A. The major difference will be that cells/batteries within this category will be tested:

(a) in the new condition - i.e. 1st. usable cycle.
(b) after every 50 charge/discharge cycles

Thus the tests will be conducted on fully charged and fully discharged cells/batteries which are:

(a) new - in their 1st usable cycle
(b) having completed 50 cycles
(c) having completed 100 cycles, and every 50th cycle thereafter until the deliverable capacity is reduced to 60% of the nominal stated output.

Cells/batteries will thus be accorded a classification based upon the most hazardous findings as described in categories A and B.

7.5.6 Group F

Rechargeable lithium cells/batteries
- housed in equipment which is being transported.

The same general ruling applies as outlined in Group C. In this case, the battery classification is derived from the considerations described under Group E.

7.5.7 Group G

Equipment (portable) employing lithium rechargeable cells/batteries, which is temporarily transported and may be used in transit.

Such batteries will be subjected to a "forced discharge test" as outlined in Group D. The major difference is that for rechargeable lithium batteries, the forced discharge test (including shock, vibration testing) will be conducted upon cycled batteries as well as new

batteries. Thus, the test will be performed on new batteries (condition as for Group D) and on batteries which have completed: 1) 50 charge/discharge cycles, 2) 100 charge/discharge cycles, 3) 150 charge/discharge cycles etc.

As described in Group D, batteries will be ascribed a classification based upon the findings of the "most potential hazard" - as referenced in Groups A and B.

7.6 Packaging

Cells and batteries, except those installed in equipment, must be packaged in a manner which prevents short circuiting. The package must be strong and rigid to prevent damage to the contents during transportation with normal handling.

A single package shall contain an aggregate quantity of lithium not greater than 500gms.

7.7 Labelling

Packages containing lithium batteries should be labelled "lithium batteries" and should display a "flammable solid" sign.

Figure 1

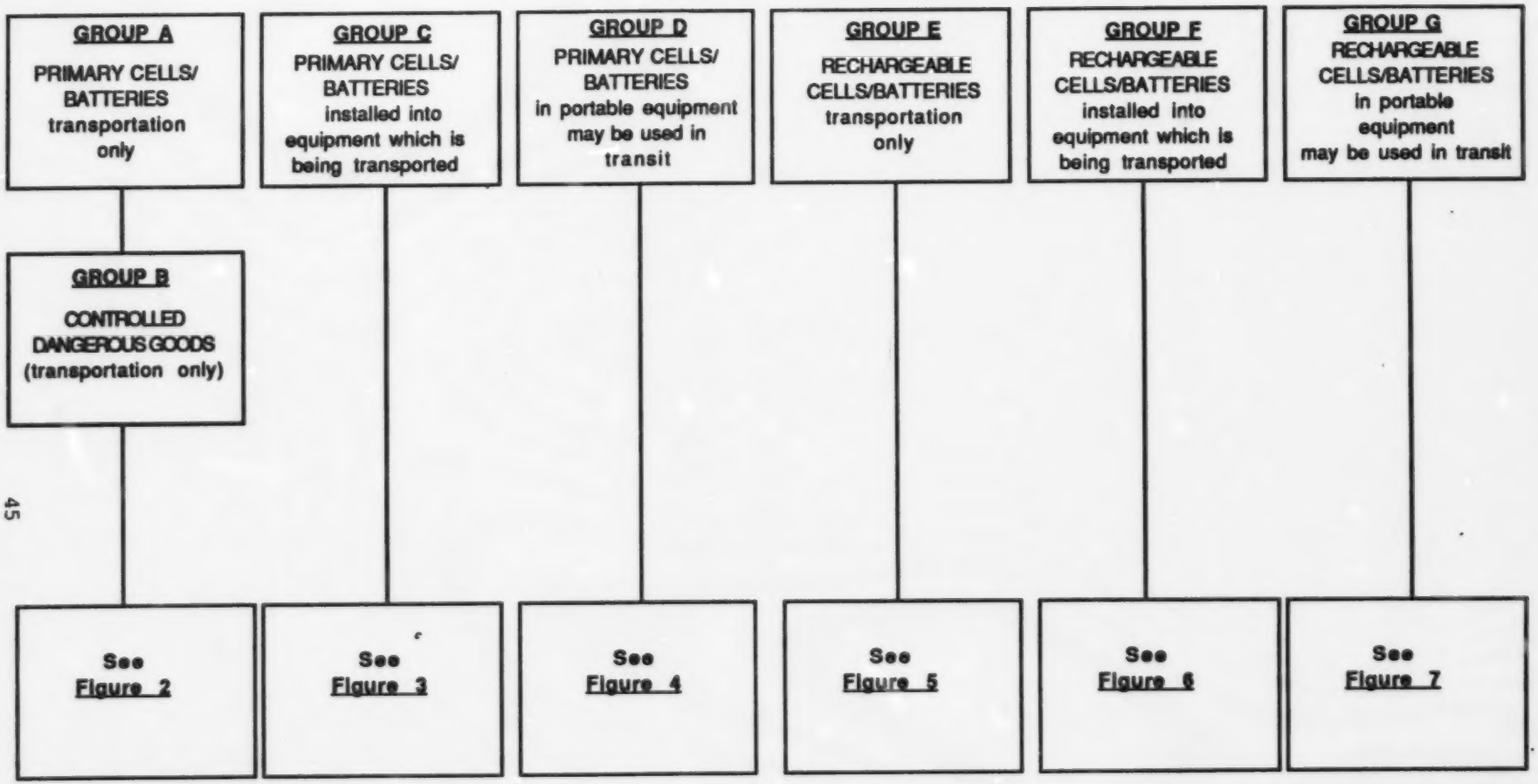
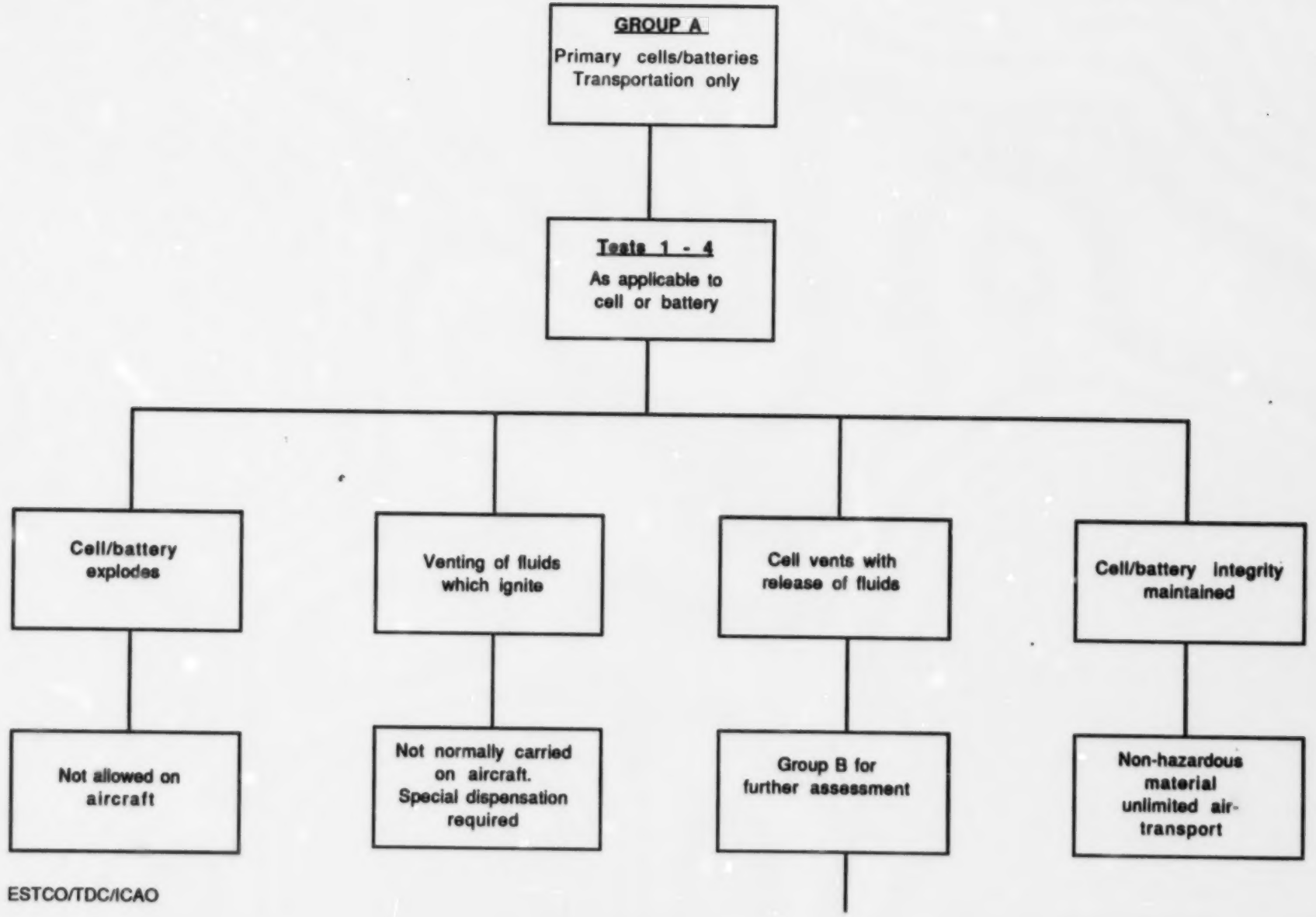
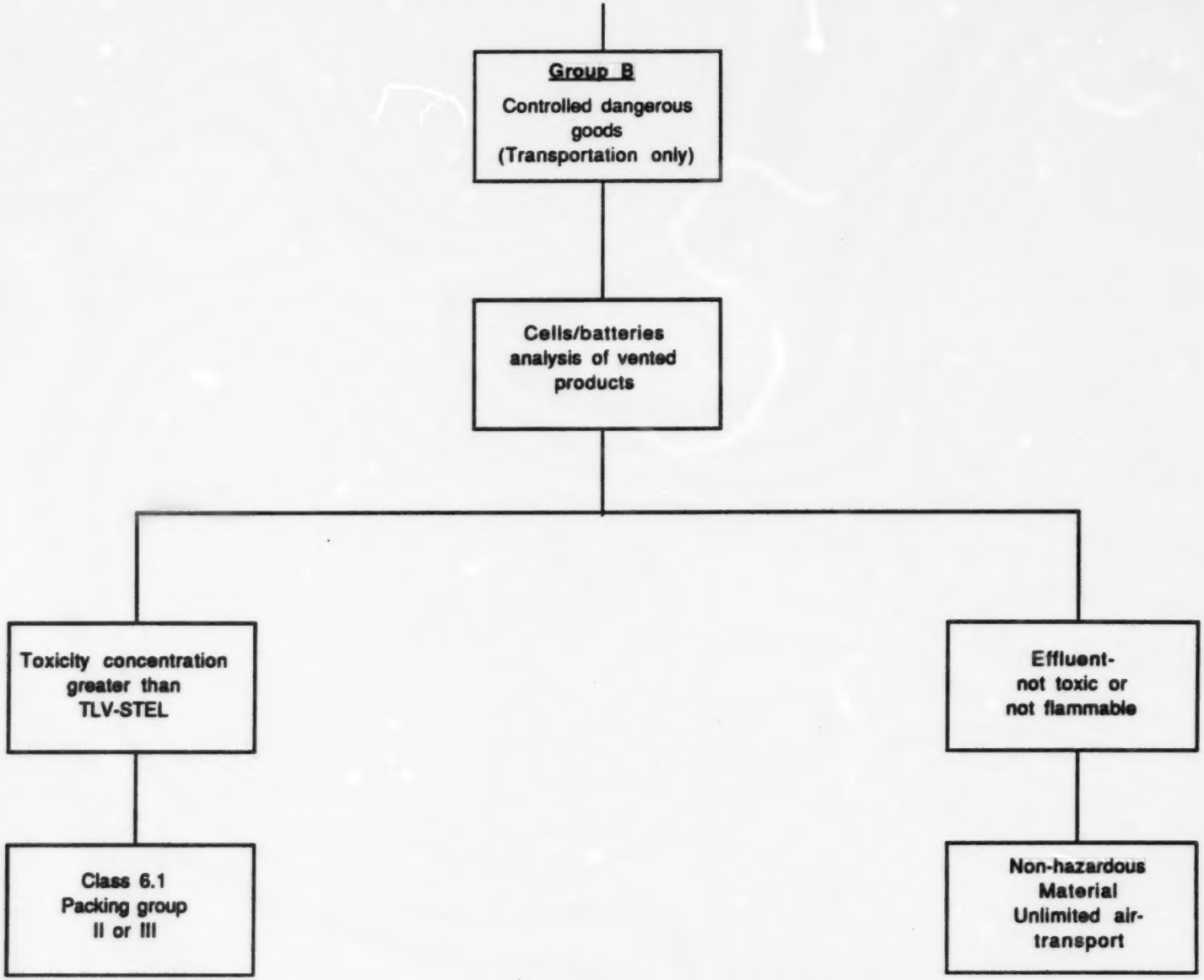

GROUP A
PRIMARY CELLS/ BATTERIES transportation only
GROUP B
CONTROLLED DANGEROUS GOODS (transportation only)
GROUP C
PRIMARY CELLS/ BATTERIES installed into equipment which is being transported
GROUP D
PRIMARY CELLS/ BATTERIES in portable equipment may be used in transit
GROUP E
RECHARGEABLE CELLS/BATTERIES transportation only
GROUP F
RECHARGEABLE CELLS/BATTERIES installed into equipment which is being transported
GROUP G
RECHARGEABLE CELLS/BATTERIES in portable equipment may be used in transit
See Figure 2
See Figure 3
See Figure 4
See Figure 5
See Figure 6
See Figure 7

Figure 2



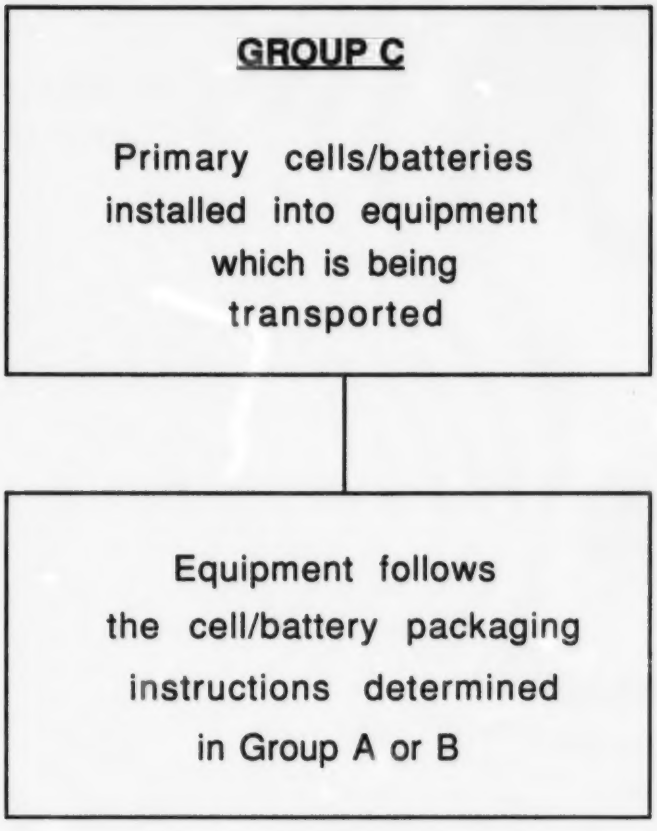
ESTCO/TDC/ICAO

Figure 2 cont'd


Group B
Controlled dangerous goods (Transportation only)
Cells/batteries analysis of vented products
Toxicity concentration greater than TLV-STEL
Effluent- not toxic or not flammable
Class 6.1 Packing group II or III
Non-hazardous Material Unlimited air-transport

ESTCO/TDC/ICAO

Figure 3


GROUP C
Primary cells/batteries installed into equipment which is being transported
Equipment follows the cell/battery packaging instructions determined in Group A or B

ESTCO/TDC/ICAO

Figure 4

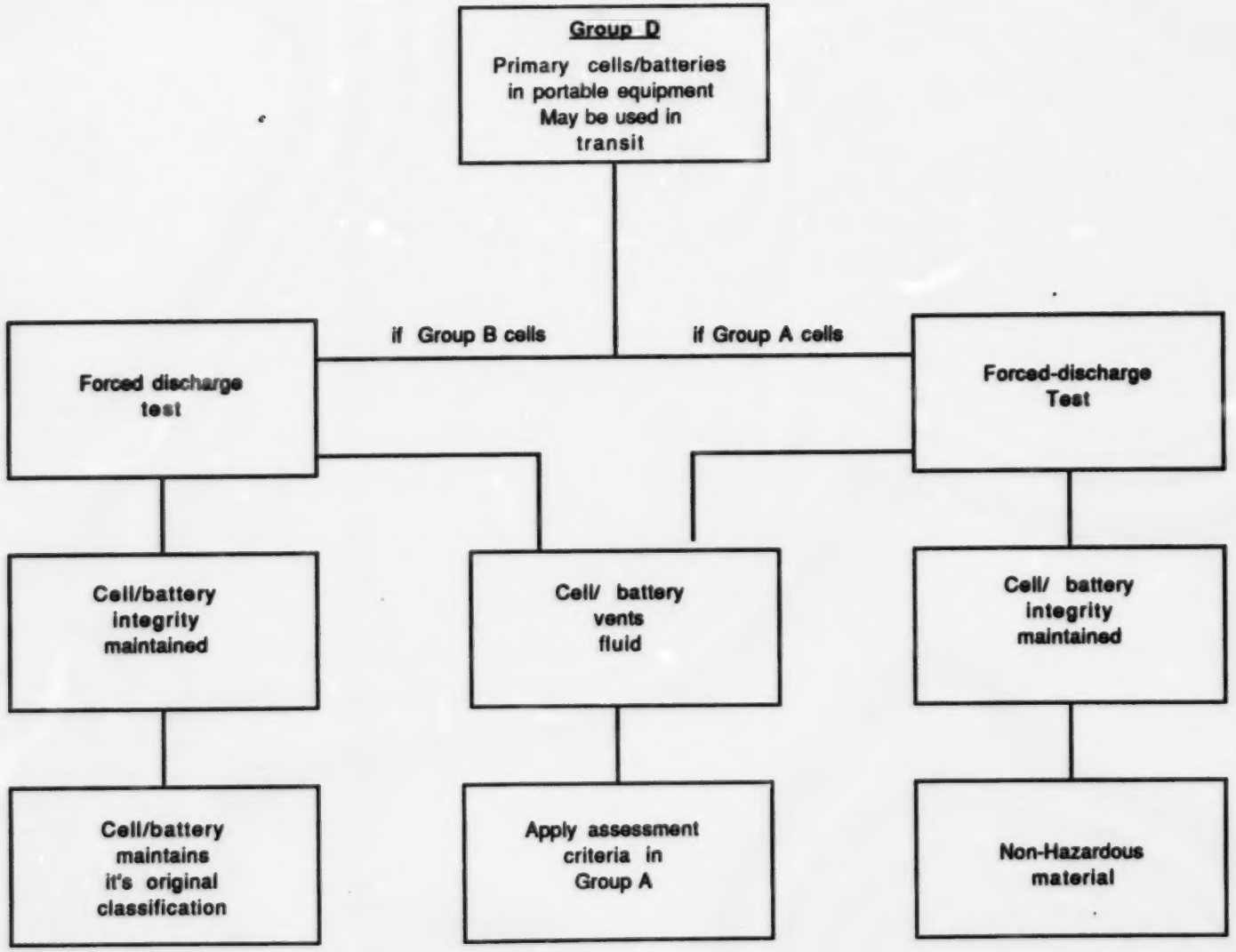

Group D
Primary cells/batteries in portable equipment May be used in transit
if Group B cells
if Group A cells
Forced discharge test
Forced-discharge Test
Cell/battery integrity maintained
Cell/ battery vents fluid
Cell/ battery integrity maintained
Cell/battery maintains it's original classification
Apply assessment criteria in Group A
Non-Hazardous material

Figure 5

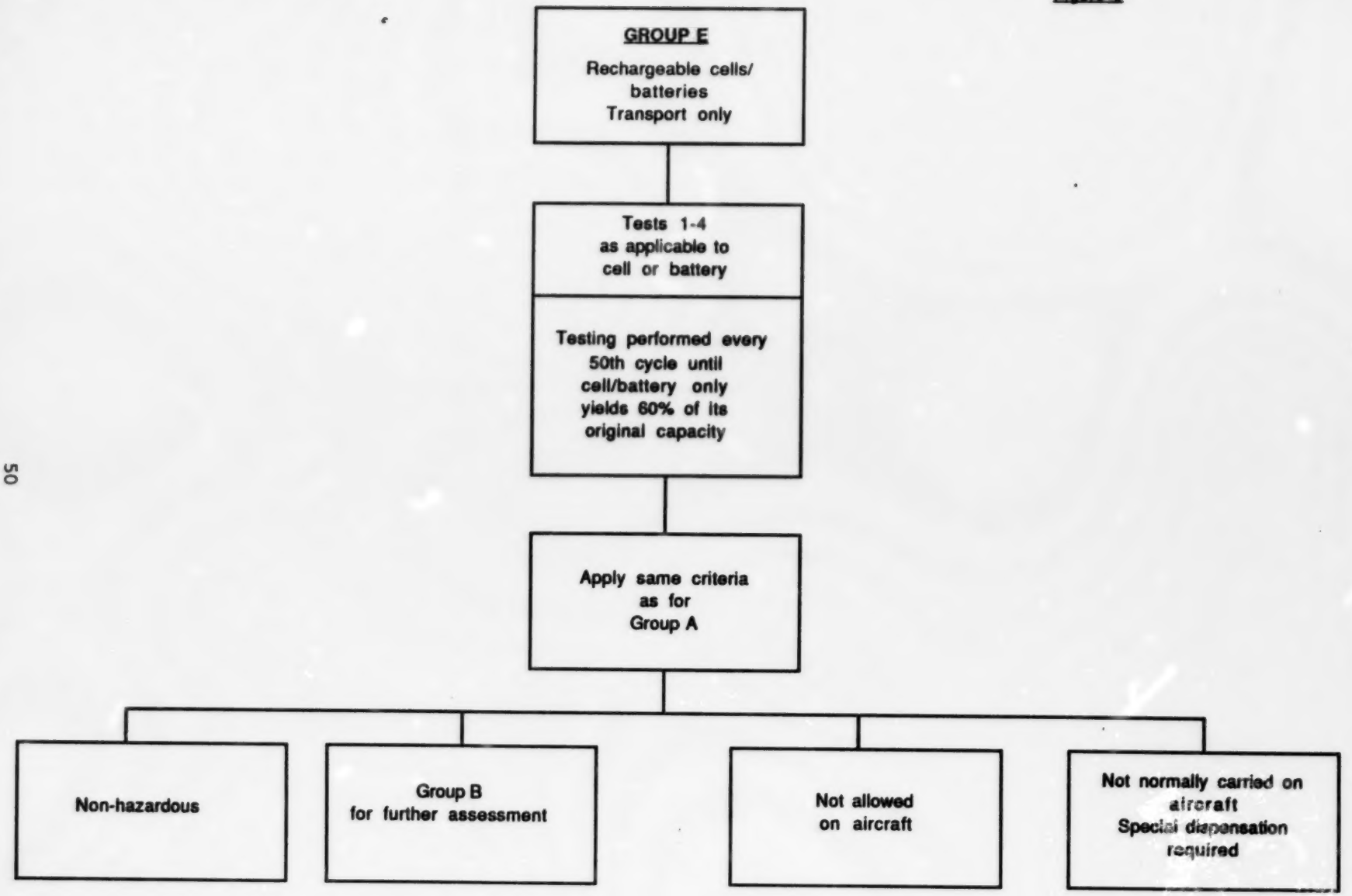
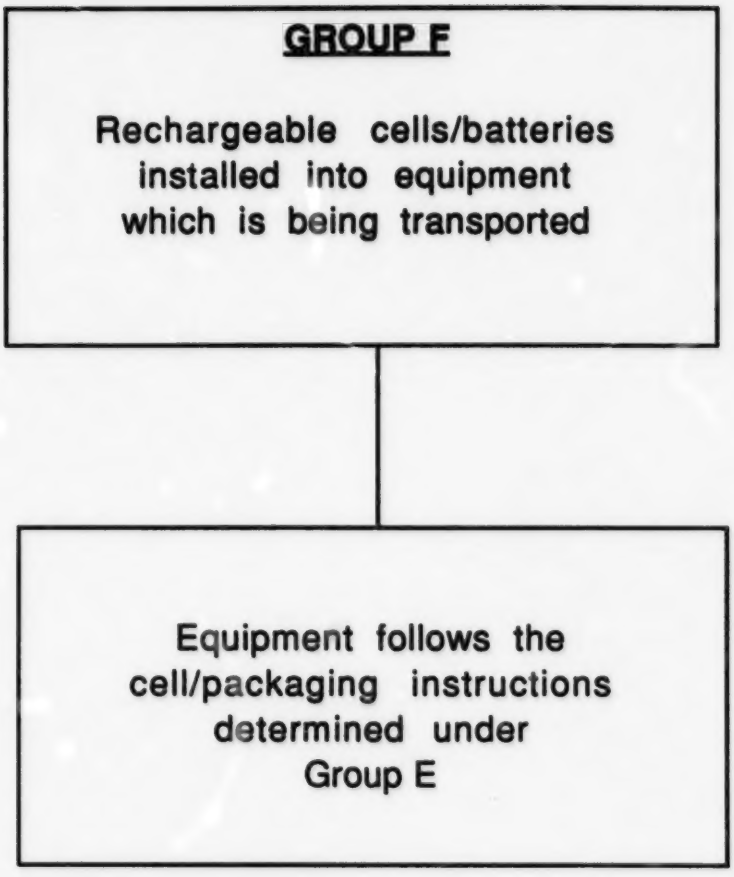
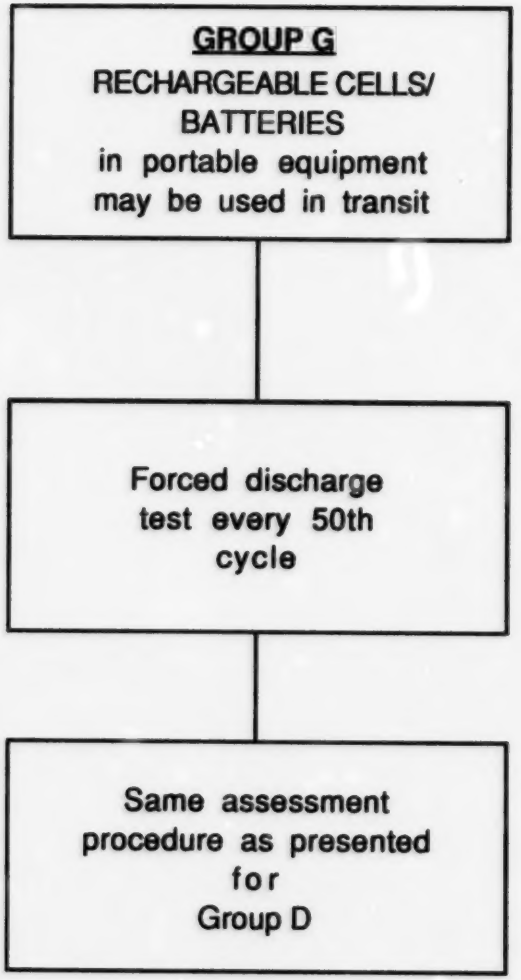

GROUP E
Rechargeable cells/ batteries
Transport only
Tests 1-4 as applicable to cell or battery
Testing performed every 50th cycle until cell/battery only yields 60% of its original capacity
Apply same criteria as for Group A
Non-hazardous
Group B for further assessment
Not allowed on aircraft
Not normally carried on aircraft Special dispensation required

Figure 6


GROUP F
Rechargeable cells/batteries installed into equipment which is being transported
Equipment follows the cell/packaging instructions determined under Group E

ESTCO/TDC/ICAO

Figure 7


GROUP G
RECHARGEABLE CELLS/
BATTERIES
in portable equipment
may be used in transit
Forced discharge
test every 50th
cycle
Same assessment
procedure as presented
for
Group D

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2. Dangerous Goods Regulations. 30th Edition, Jan. 1989. (IATA)

3. Hazardous Materials Regulations. D.O.T. E 7052 (18th revision).

4. U.S. Patent 3918610, Alcoa, Nov. 1975.

5. U.S. Patent 4556613, H. Taylor et al., Duracell, Dec. 1985.

6. G. H. Roman. Army developed and procured lithium-sulphur dioxide batteries - A military risk assessment, Dec. 1984.

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8. U.S. DOT E 9348 - response to ref. 7, Apr. 1985.

9. Sanyo brochure SF-5827.

10. Saft brochure TIM-LS8A-07/84.

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13. U.S. Patent 4307158, Thibault (G.E.), December 1981.

14. U.S. Patent 4664287, Wilson, Allvey et al. (SAFT), May 1987.

15. H. Taylor and B. McDonald. Abuse testing of lithium-sulphur dioxide cells and batteries. 27th Power Sources Conference, June 1976.

16. C. T. Havens and G. P. Misczyk. Thermal protection for lithium batteries. Lithium Battery Seminar, Florida, March 1989.

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1. Gijutsu Kaigai, Kenkyusho Shiryo. Toxic and Hazardous Industrial Chemicals Safety Manual for Handling and Disposal with Toxicity and Hazard Date, The International Technical Information Institute, copyright 1984.

2. N. Irving Sax. Cancer Causing Chemicals, Litton Educational Publishing, Inc., copyright 1981.

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6. Material Safety Data Sheets (from various suppliers).

APPENDIX I

Canadian Air Line Pilots Association

Headquarters: 1900 Steeles Avenue East, Brampton, Ontario, Canada L6T 1A2 Tel. (416) 453-8210 Fax (416) 453-8757

June 28, 1989

Mr. G. W. Allvey
GEMAG
425 Concord Drive
Beaconsfield, P.Q.
H9W 5T1

Dear Mr. Allvey,

Once again let me thank you for the time you spent in conversation with me at CALPA on the 10th of May with regards to the testing of lithium batteries. As you will recall, I expressed concern over the introduction of foreign made batteries which would not likely be subjected to the same stringent tests that are being applied to those batteries manufactured here in Canada by MOLI Energy.

I understand that the testing of the batteries is incorporated into the manufacturing process and that there are many safeguards in the cells themselves to prevent problems in the unlikely event of cell discharge or overheat. As you stated, Ni-Cad batteries went through the same teething process when they were first introduced.

As you requested I have obtained the information on natural airframe and engine frequencies for you to use in your tests. The frequencies of the airframe are:

Wing/Tail	3 to 5 cycles per second
Fuselage	Less than 10 cps
Aerodynamic	Control surface less than 12 cps

Engine rotation speeds are in the range of 5000 to 10000 RPM with a corresponding frequency range of 80 to 160 cps.

I look forward to the results of your tests and appreciate being able to give you CALPA's opinion on this type of battery.

Yours truly,

Peter Rex /ax

Captain Peter Rex
CALPA Dangerous Goods Committee Chairman

PR/bk

APPENDIX II

Transport Canada Contract.
T8200 - 9511/01 - 3D

Report on a visit to the U.S.A. - 9-12 July 1989.

CECOM - Fort Monmouth.

People seen: M. Sulkes.
J. Christopolus.
P. Lam.

The Electronics Command centre is the expertise base for batteries used by the U.S.army. Resources are allocated to researching new battery systems, design approval and first article testing. Lithium batteries used in army radio-communication sets, night vision goggles and surveillance equipment, makes this organization the biggest lithium battery consumer world wide. With so much purchasing power available to it, CECOM not only possesses in depth experience in handling large quantities of batteries but also figures prominently in cell/battery design to meet their needs.

By far, their experience is concentrated on the transportation, use and disposal of lithium-sulphur dioxide batteries. The consensus is that the latter technology has improved to the state wherein they consider the battery system extremely safe. Reported incidences - in theory, any battery mishap is a reportable incidence - have dropped from about 35 per million cells (reported in '83 for the period '78-'82) to less than 10 per million for the period to Oct '84.[1] None of these incidences has occurred during transportation of batteries.

Normal air transportation of lithium batteries is governed by AFR71-4.[2] which reqires adherence to the appropriate D.O.T. exemption. The order, however, allows field commanders to overrule this ruling in the case of tactical, contingency or exercise operations. Under this relaxed ruling, lithium batteries may be transported in pieces of equipment and spare batteries carried with the soldier in his backpack, rucksack or pockets.
A further deviation from D.O.T.E7052 (lithium battery exemption) is that of air transportation of spent/discharged batteries. Such batteries are allowed to be air transported provided that they are adequately packaged in insulating material - the same basic requirement as for new batteries. Depending upon the size of the aircraft (not the size of the lithium battery), lithium batteries are coded according to their risk assessment and generally fall into the range 1E-3E, where
E denotes the frequency of an incidence - in this case negligible.

The number denotes the hazard category, i.e.

1 - catastrophic.
2 - critical.
3 - marginal.

2.

The risk asssessment coding is derived by assuming that one cell of 8 Ah capacity (squat D cell) will vent into the aircraft and assuming the characteristics of the given aircraft, the initial sulphur dioxide concentration may be calculated. This derived concentration is then used to determine the harmful affects to personnel. The method assumes spontaneous ejection of electrolyte/cathode material and subsequent immediate diffusion to all parts of the aircraft. It ignores fresh air flow rate through the aircraft and, in consequence, the sulphur dioxide concentrations quoted will be 1) lower than actual in the immediate vicinity of the venting, and 2) higher than actual through the remainder of the aircraft.

Testing on secondary lithium cells has been performed mainly on pilot scale production models or laboratory produced models. Thus far, they have evaluated about 150 Moli Energy 'AA' sized lithium-molybdenum disulphide cells without incident. By and large, the latter cells are considered to be a safe product - even in the event of a venting wherein a "non toxic material will be emitted". CECOM have experienced one explosion with a lithium-molybdenum disulphide 'C' sized cell. They confess, however, that the cell was under a high rate charge condition and that the thermal management considerations of the larger cell are different to those of an "AA" sized cell. CECOM obviously retain a great confidence in Moli-Energy and their products in that Moli were awarded a battery development contract based upon a "C" sized cell in lithium-manganese dioxide.

D.O.T. - Washington.
Office of Hazardous Materials Transportation.

People seen: S.Hedgepeth
C.Schultz.

The D.O.T. are responsible for the rules governing the air transportation of lithium batteries. Batteries used within the aircraft fall into the jurisdiction of the FAA.
As far as the U.S. is concerned, there are no rules covering the air transportation of lithium batteries. Such carriage is permitted within the U.S. under a series of exemptions.* Whilst, in the long term, D.O.T. would like to see a clearly defined set of criteria, their workload will not allow resources to it's establishment. Their present occupation is devoted solely to evaluating submissions for the issuance of exemptions or to the renewal of exemptions (required biennially).
* An exemption is basically a permit granted to a manufacturer to allow the air transportation of his product. To obtain such

exemptions, manufacturers are obliged to submit results of electrical, environmental and abusive tests which indicate that such products will not present a safety hazard during transportation. In the main, the test program is established by the

company and approved/disapproved by D.O.T. Seemingly this office is not overly concerned that a cell may vent but must obviously guard against the possibilities of explosion, fire or the emission of toxic materials.
Although all incidences aboard aircraft should be formally reported to this office, they have never received any reports of a lithium cell/battery failure during transportation.
Incidentally, some of the criteria stated in exemption DOT-E7052 are accepted as being in need of revision. For example, the 2/3 voltage minimum requirement was based upon the experience with one lithium chemistry produced by a particular manufacturer during the late 1970s. In view of

1) Design improvements
2) The proliferation of lithium couples,

the requirement now has limited validity.

Battery Engineering Inc.

People seen: N.Marincic.

Battery Engineering was the only representative of battery manufacturers interviewed during this visit. On the whole, B.E.'s remarks centred on the confusion that exists generally on the transportation of lithium batteries. Such confusion arising from the inconsistency of road/air agencies. For example, batteries carried by air must carry a "dangerous when wet" label whilst road transport requires "flammable solid" labelling. Even now there is no UN number for the road transportation of lithium batteries. In consequence, some carriers are unsure of the rules to be adopted and refuse acceptance of such loads.
The remainder of the discussion centred on cell design criteria and it's influence on safety. In this respect, B.E.s comments/opinions were in total unison with those of the author in that:-
For a given chemistry, safety performance will be a function of

a) mechanical design - bobbin or spiral format.
b) mechanical integrity - strength of components.
c) chemical composition - relates to reaction products formed during possible overcharge/overdischarge
   - relates also to the cell impedance characteristic and it's ability to emit power.
d) thermal management problems - again this is a function of mechanical design or choice of materials.

B.E. agreed that if a cell (not containing a venting mechanism) can withstand a malfunction without causing leakage or an explosion, it is preferable not to build a venting device into the cell. A cell (within a battery pack) which vents and exudes electrolyte can result in the creation of localized "hot spots" during a battery discharge and thus initiate other possible hazards. Typically, a test to evaluate the integrity of the cell may be to heat it to (say) 70deg.C and then subject the cell to a short circuit discharge. If the resultant cell temperature is not too high (say 150deg.C), the cell does not require the inclusion of a venting system.
Similarly, B.E. agreed that the weight of lithium contained in a cell is not indicative of it's safety. The rate at which power is deliverable is a better indicator of it's safety characteristics. In consideration of the latter, a high temperature short circuit test may be a critical requirement to be adopted and included in future legislation.

B.W.Allvey

for ESTCO
Univ. of Ottawa.

1. Army developped and procured lithium sulphur dioxide batteries.
A military risk assessment. G.H. Roman. Dec.'84.

2. Preparation of hazardous materials for military air shipment.
AFR-71-4 amended 12 Sept '86.